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(54) PROCESS OF PREPARING POLYALKYLENEGLYCOL DIBENZOATES

(71) We, STAMICARON N.V., a Netherlands Limited Liability Company of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process of preparing polyalkyleneglycol dibenzoates, for instance diethyleneglycol dibenzoate, triethyleneglycol dibenzoate, and dipropylene glycol dibenzoate, from benzoic acid and a polyalkylene glycol, which are suitable for use as plasticizers, for example in the processing of polyvinyl chloride and polyvinyl acetate.

Polyalkyleneglycol dibenzoates may be obtained by reacting a glycol with benzoic acid in the presence of an acid catalyst, for instance sulphuric acid or toluenesulphonic acid. If diethyleneglycol dibenzoate for example is thus prepared, the reaction product will have a colour which makes it unsuitable for use as a plasticizer and decolorizing by fractional distillation is too expensive for practical purposes. Moreover part of the diethyleneglycol dibenzoate formed decomposes during the reaction.

Dipropylene glycol dibenzoate when prepared according to the said known method yields an acceptable product only if the esterification is limited to not more than 50 %, and if in fact the esterification is continued to about 80 % by removal of the reaction water, the reaction does not proceed further and the reaction product is unacceptable as a plasticizer.

It has been suggested that such disadvantages can be obviated by reacting benzoyl chloride, instead of benzoic acid, with the polyalkylene glycol, and removing the resulting hydrogen chloride during the reaction. Although this method yields a suitable reaction product, the plant required to handle

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the hydrogen chloride formed in the reaction is expensive, and benzoyl chloride is considerably more expensive than bezoic acid.

It has now been found that polyalkyleneglycol dibenzoates can expeditiously be prepared by reacting benzoic acid with the glycol concerned without the need of an acid catalyst, and that in this way a product can be obtained that does satisfy the colour standards set for plasticizers. The process according to the invention comprises effecting the reaction between the polyalkyleneglycol and the bezoic acid at a temperature between 200 and 300°C. and removing reaction water from the reaction mixture during reaction by evaporation.

Surprisingly in the process according to the invention the use of the relatively high temperatures does not have an adverse influence on the colour of the reaction product. A sufficiently high reaction rate and a very good yield can be obtained with avoidance of the use of a catalyst while no special measures are required for removing the reaction water.

The preferred temperatures used in the process according to the invention are between 210 and 265°C, whereby an optimum reaction rate and yield may be obtained.

The process according to the invention may be carried out with the use of equivalent amounts of benzoic acid and polyalkylene glycol. In practice, however, a small excess of the benzoic acid is used to effect a complete esterification.

In the process according to the invention pressure is not a critical factor, so that for reasons of economy atmospheric pressure may be applied. If so desired the final stage of the reaction may be effected under a slightly reduced pressure so as to facilitate the removal of the reaction water to ensure the completest possible esterification.

After termination of the esterification pro-

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cess, the resulting reaction product can be worked up by subjecting it to an alkaline washing followed by drying, for instance by heating at reduced pressure or by an azeotropic distillation with benzene or other suitable solvents.

Unused benzoic acid, if any, can be recovered by acidifying the washing liquid obtained in the alkaline washing of the crude 10 reaction product.

The benzoic acid used in the process according to the invention need not be pure, and while a coloured reaction product may consequently be obtained, it has been found 15 that this product can effectively be decoloured by treating it with a mild oxidation agent, for instance a dilute acidic or basic potassium permanganate solution. Decolouration with a basic permanganate solution 20 may be combined with the washing of the crude reaction product if so desired. If an excess amount of impure benzoic acid is used, the recovered benzoic acid appears to be chemically pure.

25 The process according to the invention can be carried out as a continuous or as a batch process.

The following Examples of the invention are provided.

30 *Example I*

134 grams of dipropylene glycol (1 mole) and 256 grams of chemically pure benzoic acid (2.1 moles) were introduced into a 1-litre flask equipped with a stirrer, a gas inlet tube and a distilling head. The mixture in the flask was rapidly heated under nitrogen to about 210 °C and with continued stirring and introduction of nitrogen, the temperature was gradually raised to 255 °C over a period of 3 hours and maintained at this temperature for a further 3 hours, 36 grams of reaction water distilling over.

The resulting reaction mixture was cooled to about 85 °C and washed at this temperature with 100 millilitres of 1 % by weight sodium hydroxide solution, 200 millilitres of 5 % by weight sodium carbonate solution, and twice with 100 millilitres of water, in that order.

50 After drying of the reaction product by azeotropic distillation with benzene, 310 grams of dipropylene glycol dibenzoate was obtained, having a colour 58 °Hazen, an acid number 0.003 mgeqs. per gram and n_{D}^{20} 1.5278.

The water layers obtained in the washings with the sodium hydroxide solution and the sodium carbonate were combined and acidified with sulphuric acid. The benzoic acid 60 precipitated in this treatment was washed with water and dried. 31 grams of benzoic acid were obtained.

The efficiency of the ester preparation was 98 % based on the benzoic acid reacted, and 91 % based on the original

amount of dipropylene glycol.

Example II

Dipropylene glycol dibenzoate was prepared as in Example I, except that technical grade benzoic acid, obtained by oxidation of toluene was used instead of chemically pure benzoic acid. The said technical grade benzoic acid has an unpleasant smell and was yellow in colour. The washing yielded a green reaction product with an 75 efficiency of 90 % based on the dipropylene glycol. The washed reaction product was then decoloured by slowly adding at about 80 °C and with stirring, a solution consisting per 100 grams of reaction product, of 1 80 gram of potassium permanganate and 4 grams of sulphuric acid in 100 millilitres of water. The aqueous liquid layer was separated from the ester layer and the ester is washed with water.

85 After drying, by heating at reduced pressure, and filtration, the resulting dipropylene glycol dibenzoate was almost completely decoloured (colour 50 °Hazen, acid number 0.005 mgeqs. per gram, and n_{D}^{20} 90 1.5269).

Example III

Example II is repeated, except that decolouration was effected with a solution of 1 gram of potassium permanganate and 5 95 grams of sodium carbonate in 100 millilitres of water. The resulting product was almost colourless (colour 70 °Hazen).

Example IV

100 100 grams of diethylene glycol (1 mole) and 256 grams of chemically pure benzoic acid (2.1 moles) were introduced into a 1 litre flask equipped with a stirrer, a gas inlet tube and a distilling head. The mixture in the flask was rapidly heated to 210 °C 105 under nitrogen with stirring. With continued stirring and introduction of nitrogen, the temperature was gradually raised to 260 °C over a period of 3 hours and the mixture maintained at this temperature for 110 2 further hours. A total of 34 grams of reaction water being distilled over.

The resulting reaction mixture was worked up in the same way as in Example I. The yield was 288 grams of diethylene 115 glycol dibenzoate (colour 66 °Hazen, acid number 0.005 mgeqs. per gram and n_{D}^{20} 1.5420).

Based on the original amount of glycol, the efficiency was 91 % and based on the 120 benzoic acid reacted.

Example V

Example IV was repeated, except that technical-grade benzoic acid was used instead of chemically pure benzoic acid. The 125 resulting green reaction product was decoloured with a solution of 1 gram of potassium permanganate and 5 grams of sodium carbonate in 100 millilitres of water, at about 85 °C. The colour of the resulting 130

diethyleneglycol dibenzoate was 26 "Hazen (n_D²⁰ = 1.5421).

Example VI

150 grams of triethyleneglycol and 256 5 grams of technical-grade benzoic acid were introduced into a 1 litre flask equipped with a stirrer, a gas inlet tube and a distilling head. The mixture in the flask was rapidly heated to 210 °C with stirring under nitrogen. With continued stirring and introduction of nitrogen, the temperature was gradually raised to 250 °C over a period of 3 hours and the mixture maintained at this temperature for 2 further hours. At the 15 end of this period a total of 35 grams of water has been distilled over.

The resulting reaction mixture was washed in the same way as described in Example I, to provide 31 grams of pure 20 benzoic acid in the aqueous washing liquid. A brown product was obtained, which was decoloured by treatment with a solution of 1 gram of potassium permanganate and 5 25 grams of sodium carbonate in 100 millilitres of water at about 90 °C.

After washing and drying there results 340 grams of white triethyleneglycol dibenzoate, having a melting point of 48-48.5 °C (acid number 0.002 mgeqs. of acid per 30 gram). The efficiency was 97 % based on the reaction of technical-grade benzoic acid, and 92 % based on the original quantity of glycol.

WHAT WE CLAIM IS:—

1. A process for preparing a poly-35 alkylene dibenzoate, comprising reacting a polyalkylene glycol with benzoic acid at a temperature between 200 and 300 °C, and removing the reaction water from the reaction mixture by evaporation during the 40 reaction.

2. A process according to Claim 1, in which the reaction is effected at a temperature between 210 and 265 °C.

3. A process according to Claim 1 or 45 Claim 2, in which the reaction product is subjected to treatment with a mild oxidation agent.

4. A process according to Claim 3, in which the mild oxidation agent is a dilute 50 acidic or basic potassium permanganate solution.

5. A process of preparing a polyalkylene-glycol dibenzoate, substantially as hereinbefore described in the Examples. 55

6. A polyalkyleneglycol dibenzoate obtained according to a process according to any one of the preceding claims.

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